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THE EFFECT OF LSM CORROSION PROTECTION ON AL ALLOYS

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ABSTRACT

Laser surface treatment has been recognized as a useful method for corrosion protection of surfaces as a result of improved microstructure/phase formation and compositions. Therefore, Laser surface treatment techniques, including laser surface melting (LSM) has been the subject of considerable interest as a means of enhancing the corrosion performance of aluminum alloys.

In this research, disc samples of (7075, 6061 and 5083) aluminum alloys have been prepared, polarization tests were carried out under static condition in a different concentration of NaCl solution (1.5, 2.5, 3.5) %wt at 25^{o}C. The experiments were carried out before and after laser surface melting by (Nd: YAG, MED-810) pulse laser, system (Q-Switched Nd: YAG 1064/532nm)

After the laser melting, the surface showed a significant reduction in the number of large intermetallic particles and relatively homogenous melted layer generated that provided significant improvement in the resistance of the alloy against corrosion, as assessed by corrosion test and X-RAY Diffract (XRD) test.

Key words: Aluminum, Corrosion. Laser, Polarization, Potentiodynamic

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1. INTRODUCTION

Aluminum alloys are frequently used in industrial application due to their low density, favorable mechanical properties, and excellent corrosion resistance.

In the presence of chloride ions with a very deteriorating action, the protective property of a passive/oxide film at the surface of specimens made of aluminum alloys is drastically reduced, which results in big corrosion damages of small surface pits. This type of corrosion is referred to as pitting corrosion [Ezuber, 2007].

To reduce surface damage on the parts exposed to work under demanding conditions, an adequate surface treatment and protection is essential. More recently, there has been a growing interest in improving the corrosion performance of aluminum alloys by laser techniques. The techniques principally involved are laser surface melting (LSM), laser surface alloying (LSA) and laser surface cladding (LSC).

However, one of the non-traditional surface engineering techniques, laser surface melting (LSM), has attracted growing interest in recent years for its ability to improve the corrosion performance of aluminum alloys.

LSM is a versatile and promising technique that can be used to modify the surface properties of a material without affecting its bulk properties [Polmear, 1996] [Kammer, 1999].

However, the outstanding features of the laser surface modification (LSM) technique include the ability to promote better chemical and structural uniformity on the surface of a bulk material to eliminate or minimize heterogeneities, and to facilitate mixing and quenching within the melted layer that may create a super-saturated solid solution in an otherwise immiscible solid. The creation of these types of surfaces by rapid solidification is primarily dependent upon alloy composition, structure and other properties.

Indeed, using LSM as a means for improving the corrosion resistance of metals and alloys has been widely investigated for many years.

It has been demonstrated that this technique is effective in improving the surface properties such as corrosion and erosion for many materials so an increase in the corrosion resistance of Al- Si alloys after laser surface melting was observed by Wong and co-workers [Wong & Liang, 1997]. They proved that the pitting corrosion of the laser-surface- melted Al alloys is improved.

[Chong et al., 2003] studied the corrosion behavior of Al-2014 alloy after laser surface melting. Laser surface melting was carried out using a 3 kW CW Nd: YAG laser. After the corrosion tests, they found a large number of pits, randomly distributed on the surface of as-received Al2014 alloy before LSM.

After LSM, pits formed on the laser-melted surfaces are shallower than that in the as- received alloy.

[Paul,2003] studied the polarization behavior of Al-Si alloy in 10 wt% HCl ,5 wt% NaCl solutions, they showed that the improvement in the corrosion and wear resistance using laser surface melting (LSM) is significant potential for improving surface properties.

[Chan et al, 2004] studied the effect of the excimer laser surface melting on the aluminum alloy 8090. The work has been conducted with the aim of improving the intergranular corrosion resistance of the alloy. Both the results of the electrochemical and the intergranular corrosion cracking immersion tests show that the laser treatment significantly increases the intergranular corrosion resistance of the alloy.

[Yue et al.2006] his research on Nd-YAG laser surface treatment conducted on 7075 aluminum alloy with the aim of improving the stress corrosion cracking resistance of the alloy. The results of the stress corrosion test show that untreated

specimen had been severely attacked by corrosion, with intergranular cracks having formed along the planar grain boundaries of the specimen. In contrast, only few short stress corrosion cracks appeared in the treated specimen, indicating an improvement in corrosion initiation resistance.

[Xu et al., 2006] dealt with Nd: YAG laser surface melting of aluminum alloy 6013 for improving pitting corrosion fatigue resistance in the presence of chloride-containing media. They reported that the corrosion fatigue life of the laser-surface melted Al 6013 alloy is two times longer than that of the as-received Al alloy. Also, the corrosion current for the laser-surface melted Al 6013 alloy is considerably lower than that for the as-received Al 6013 alloy.

Laser surface melting (LSM), using an excimer laser, has been employed to modify the near-surface microstructure of AA2024 aluminum alloy by Y. Yuan et al [Yuan, 2008]. They found that LSM significantly modifies corrosion attack of AA2024 alloy therefore no intergranular corrosion was readily evident in the laser melted layer, in contrast to severe pitting corrosion and intergranular corrosion observed for the as-supplied alloy.

According to the study of [Ryan and Pragnell, 2008] using the technique of pulsed laser surface melting (PLSM), they showed that the increase in the corrosion performance of pulsed laser-treated alloys has been widely attributed to the formation of a surface layer that is much more chemically homogenous than the bulk material. It has generally been assumed that the laser treatment removes second phase particles and partitionless re-solidification of the layer occurs.

[Trdan et al., 2009] investigate the corrosion behavior of the Al-Si-Mg-Mn laser-shock-processed (LSP) aluminum alloy in 3.5% NaCl water solution. Surface conditions after corrosion tests at different pulse density levels were evaluated. They proved that the pitting potential - E_{pit} increases with an increasing overlap-pulse density level so the specimen treated with 900 pulses/cm^2 showed an increase in the pitting potential of +62 mV. The specimens treated with 2500 pulses/cm^2 showed an increase in the pitting potential of +120 mV compared to the same material in the as delivered state.

[Coy et al., 2010] their research dealt with excimer laser surface melting (LSM) of the die cast AZ91D magnesium alloy which was investigated in terms of microstructure and corrosion behavior. Excimer LSM of the alloy resulted in a highly homogeneous and refined melted microstructure, which improved the corrosion resistance of the alloy.

[Pariona et al., 2012] reported a study of the laser treatment by irradiating Al–1.5 wt.%Fe alloy with Yb-fiber laser beam to investigate the corrosion behavior in an aerated H_2SO_4 solution. They found that the Yb-fiber laser beam modified the sample surface microstructure, refined the grains, formed different intermetallic phases and homogenized segregated elements. This treatment increased the corrosion resistance by about 12 to 14 times when compared to the base alloy material.

[Ahmed, 2013] deals with the effect of some variables on corrosion of 2024 aluminum alloy protected by laser technology. The electrochemical behavior of Al alloy in (NaCl) solution of different concentrations and temperatures was studied. He found that no pitting corrosion was observed on the sample after laser surface treatment and breaking potential was not reached till +400 mv.

2. EXPERIMENTAL PROCEDURE

2.1. Test material

Commercial 7075, 6061 and 5083 aluminum alloys were supplied in the form of 2 mm-thick and 25 mm diameter discs; the chemical composition of the alloys, analyzed by the “Specialized Institute of Manufacture Engineering” shown in Table (1):

Table (1) Spectrographic composition of aluminum alloy (wt. %)

Elements	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Al
5083	0.2	0.4	0.1	0.3	3.6	0.1	0.0	0.02	Bal.
6061	0.8	0.7	0.30	0.15	1.2	0.13	0.25	0.02	Bal.
7075	0.08	1.17	1.50	0.04	2.81	0.19	5.82	0.02	Bal.

2.2. Samples Preparation

The surface of the sample was ground by employing emery paper with grade numbers of 400, 600, 800, 1000 and 1500 using grinding machine (KNUTH-ROTOR 2).

Then the sample was polished using (Dimond) by a polishing machine (polisher ECOMETIII) and then cleaned with distilled water and ethanol.

2.3. Laser Surface Melting

LSM was conducted in the ambient environment, the specimens were irradiated by using (Nd-YAG, MED-810) laser system (Q-Switched Nd: YAG 1064/532nm). The specimens were placed at distance of 12 cm.

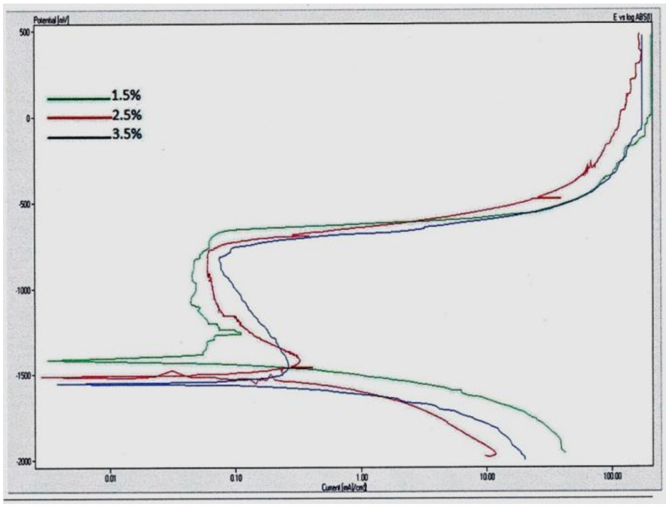
2.4. Corrosion test

In order to evaluate the electrochemical properties of various treated specimens, potentiodynamic polarisation was performed in 1.5, 2.5 & 3.5%wt NaCl solution at 25 ºC, using M lab potentiostat / galvanostat and a conventional three-electrode cell employing a graphite counter electrode and a saturated calomel reference electrode (SCE). Polarization was carried out from (-2000 to +500) v with scan rate of 20 mv/min

3. RESULTS AND DISCUSSION

3.1. Corrosion Evaluation

The first set of these results is presented in Figures (1) which show the influence of concentrations 1.5, 2.5 & 3.5 %wt NaCl solution on the corrosion behavior of 7075, 6061 and 5083 aluminum alloys respectively at 25^{o}C.



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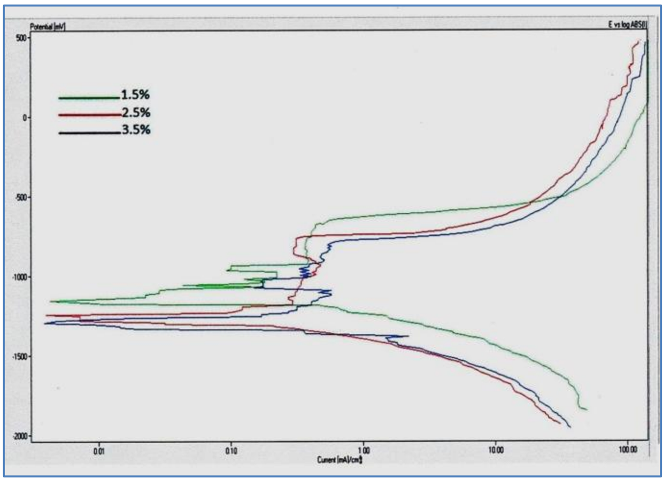

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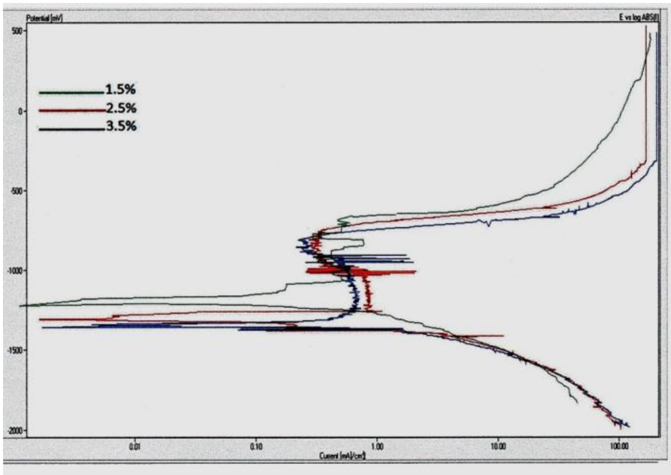


(c)

Figure (1) Polarization curves at 25 ºC and (1.5, 2.5&3.5) % NaCl for a) 7075 b) 6061 c) 5083aluminum alloys before laser surface melting.

Table (2) The variation of (E_{corr}) for the aluminum alloys at different concentrations before laser surface melting.

NaCl conc. / Aluminum alloys	1.5%	2.5%	3.5%
7075	-1410.5	-1506.4	-1520.6
6061	-1230.3	-1275.1	-1302.6
5083	-1284.3	-1325.2	-1341.8

The effect of Cl^- concentration on corrosion potential at 25^{o}C is shown in Table (2). The higher the Cl^- ions concentration results in the more negative direction of the corrosion potential of aluminum alloys.

However, aggressiveness of chloride ionsis due to: their small size, high diffusivity and strong anionic nature and very high solubility of chloride salt.

So, the increasing of NaCl concentration will increase the electrical conductivity of the solution due to increase in the number of ions present [Lifka, 2005].

Table (3) the variation of (E_{pit}) for the aluminum alloys at different concentrations before laser surface melting.

NaCl conc. / Aluminum Alloys	1.5%	2.5%	3.5%
7075	-720	-770	-790
6061	-701	-760	-791
5083	-720	-763	-800

Table (3) shows the great effect of Cl^- concentration on pitting corrosion potential at 25^{o}C. It can be seen that the higher the Cl^- ions concentration, the more negative the pitting potential (E_{pit}) of aluminum, which indicates that the increase in Cl^- concentration leads to the decrease in the electrochemical stability of aluminum because the Halides, particularly the chloride ion, are corrosive to aluminum.

However the breakdown potential (E_{pit}) shifts to more negative values as Cl^- concentration increases, this is because the breakdown of passivity is directly affected by (Cl^-) at certain temperature. These results are in agreement with those of many workers [Revie, 2008] [Subhasisa, 2012] [Szklarska, 1986].

Moreover increasing the (Cl^-) leads to increase the conductivity of the solution as cited before and as a result the corrosion current density will increase also as shown in table (4). This is in agreement with many workers [Malik, 1992] [Uhlig, 1984]. So it can be seen that, for all samples studied, the value of the corrosion current density obviously increases with increasing the concentration of NaCl from 1.5% to 3.5%.

Table (4) The variation of corrosion current density (mA/cm^2) for the aluminum alloys at different concentrations before laser surface melting.

NaCl conc. / Aluminum alloys	1.5%	2.5%	3.5%
7075	23.32 x10-3	97.48 x10-3	133.57 x10-3
6061	3.99 x10-3	43.84 x10-3	79.34 x10-3
5083	27.06 x10-3	41.55 x10-3	70.65 x10-3

Table (5) displays variations of the corrosion rate of aluminum alloys with the different concentrations of NaCl. As can be seen, the corrosion rate increases with the increase in NaCl concentrations.

Table (5) The variation of corrosion rate (gmd) for the aluminum alloys at different concentrations before laser surface melting.

NaCl conc. / Aluminum alloys	1.5%	2.5%	3.5%
7075	18.8x10^{-4}	78.5x10^{-4}	107.6x10^{-4}
6061	3.21 x10^{-4}	34.8 x10^{-4}	63.9 x10^{-4}
5083	21.8x10^{-4}	33.4x10^{-4}	56.9 x10^{-4}

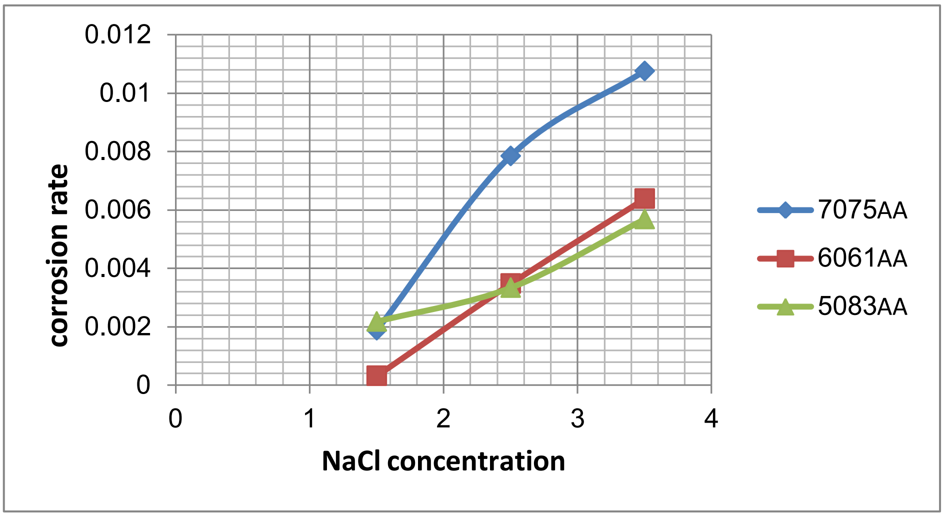
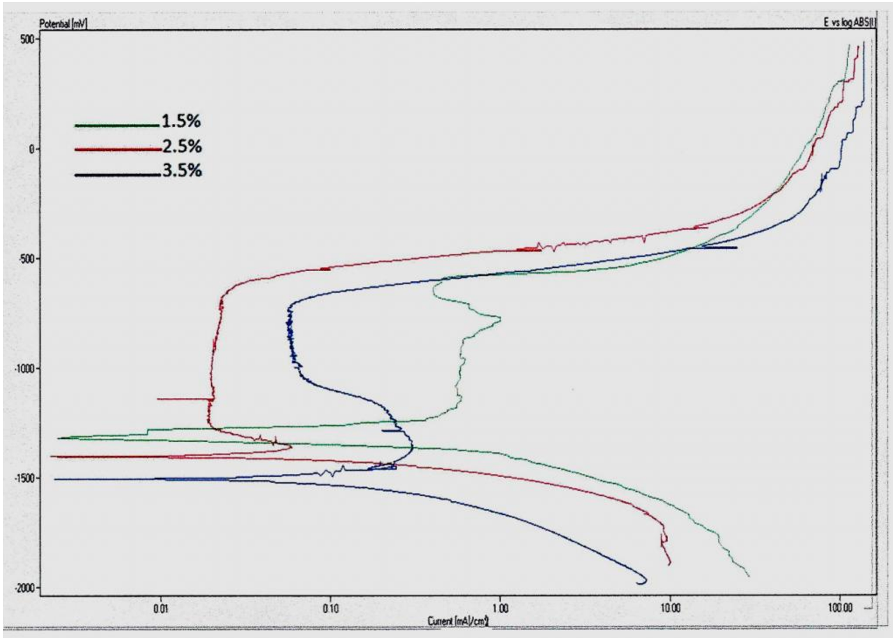


Figure (2) Correlation between corrosion rates and concentrations for different aluminum alloys

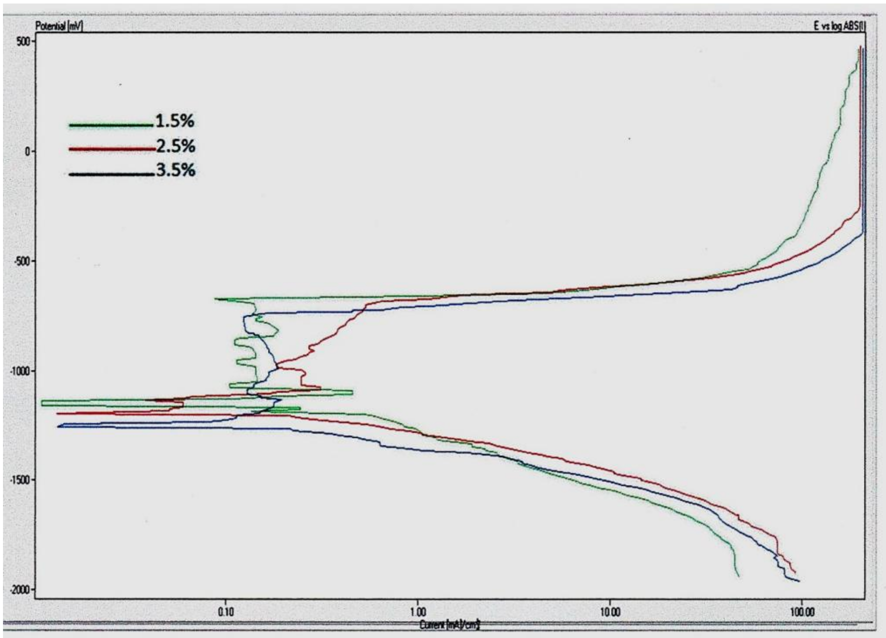
From Figure (2) which represents the correlation between corrosion rate and NaCl concentration for specimens; it is found that corrosion rate for the specimen 7075 is larger than that of 6061 and 5083 aluminum alloys under the same conditions. So it means that the specimens 6061 and 5083 have high resistance to this type of solution that results from the presence of magnesium as alloying element which improves the

corrosion resistance of these alloys. As well as the addition of zinc in 7075 aluminum alloys will reduce the corrosion resistance of aluminum alloys [Hollingsworth and Hunsicker 1992][Davis, 1999].

The second set of these results is presented in Figures (3) which show the influence of laser surface meltingtreatmenton the samples by using Nd-YAG laser in 1.5, 2.5 & 3.5 %wt NaCl solution at 25°C.



(a)



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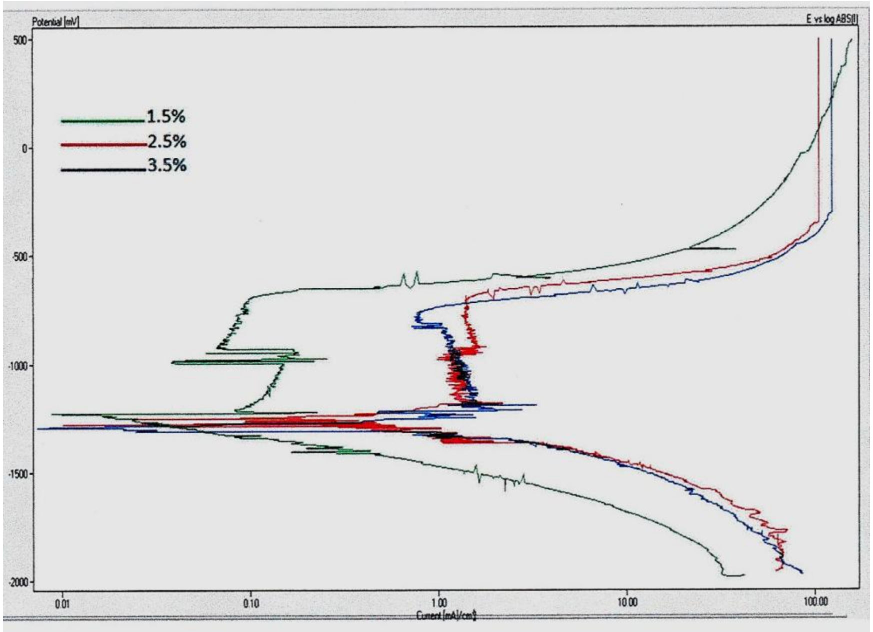


(C)

Figure (3) Polarization curves at 25 °C and (1.5, 2.5&3.5) % NaCl for a) 7075 b) 6061 c) 5083aluminum alloys after laser surface melting.

Table (6) corrosion potential (E_{corr} mv) at various concentrations for different aluminum alloys *before* and after (LSM)

Al-alloys	**7075**		**6061**		**5083**	
Conc.	**Before LSM**	**After LSM**	**Before LSM**	**After LSM**	**Before LSM**	**After LSM**
1.5%	-1410.5	-1311.1	-1230.3	-1160.5	-1284.3	-1237.2
2.5%	-1506.4	-1460.7	-1275.1	-1221.7	-1325.2	-1284.0
3.5%	-1520.6	-1498.7	-1302.6	-1247.5	-1341.8	-1302.6

From table (6) it can be seen that the corrosion potential was shifted to more positive direction indicating lower anodic rate of reaction i.e, the anodic dissolution of aluminum after LSM was lower than that before LSM.

Table (7) Pitting corrosion potential (E_{pit} mv) at various concentrations for different aluminum alloys *before* and after (LSM).

Al-alloys	**7075**		**6061**		**5083**	
Conc.	**Before LSM**	**After LSM**	**Before LSM**	**After LSM**	**Before LSM**	**After LSM**
1.5%	-720	-572	-701	-679	-720	-688
2.5%	-770	-670	-760	-720	-763	-713
3.5%	-790	-706	-791	-750	-800	-760

From table (7) it can be seen that, for all samples, the pitting corrosion potential after laser surface melting obviously shifted to more positive direction for all

aluminum alloys in different concentrations of the NaCl solution at constant temperature.

Table 8 Corrosion current density (I_{corr} mA/cm^2) at various concentrations for different aluminum alloys *before* and after (LSM).

Al-alloys	7075		6061		5083	
Conc.	Before LSM	After LSM	Before LSM	After LSM	Before LSM	After LSM
1.5%	23.32 x10-3	6.66 x10-3	3.99 x10-3	1.15 x10-3	27.06x10-3	11.95x10-3
2.5%	97.48 x10-3	27.23 x10-3	43.84 x10-3	13.32 x10-3	41.55x10-3	15.18x10-3
3.5%	133.57 x10-3	44.66 x10-3	79.37 x10-3	24.08 x10-3	70.65x10-3	23.31x10-3

Table (8) shows the great effect of laser surface melting on corrosion current densities for different aluminum alloys. It is evident that the Nd: YAG laser surface melting significantly reduced corrosion current density by as much as three times. Such improvement of corrosion performance is considered to be associated with the dissolution/removal of the large intermetallic particles, as a result of extreme high cooling rates produced by Nd: YAG laser radiation which led to further shifts of the corrosion current density toward lower values.

Therefore, the value of the corrosion rate of laser-treated alloy is smaller than that of the untreated. This occurs due to the presence of an oxide layer and because of the other phases produced by heat treatment with laser, turning this layer more resistant to the corrosion when compared to the oxide film formed on the surface of the untreated alloy during the interval of stabilization of the corrosion potential.

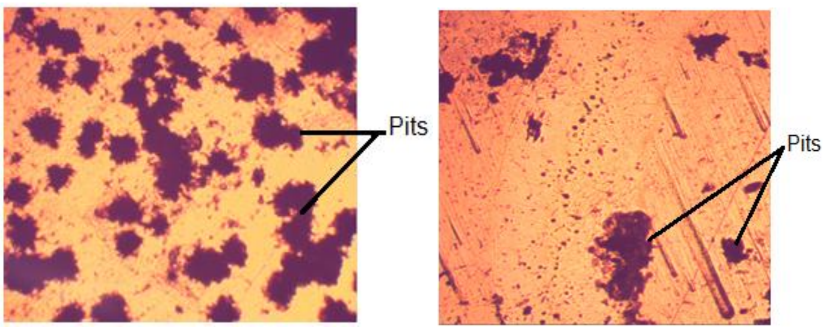
3.2. Tests on Aluminum Sample

Tests were carried out on the samples before and after laser surface melting they include, Optical microscope and X-Ray diffraction.

3.2.1. Optical Microscope Pictures Test

Photo of the sample surface was captured before and after laser surface melting. Figure (4) shows the photo after polarization (a) before laser surface melting (b) after laser surface melting

Comparing Figure (4) a) and b) indicates that (LSM) alloy has more resistance to corrosion than that without (LSM).

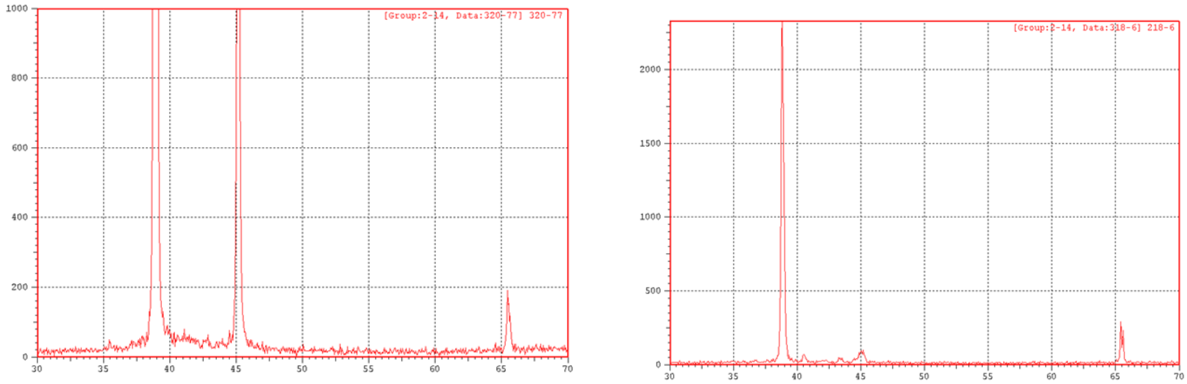


(a) (b)

Figure (4) surface of the sample after polarization (a) before laser surface melting (b) after laser surface melting

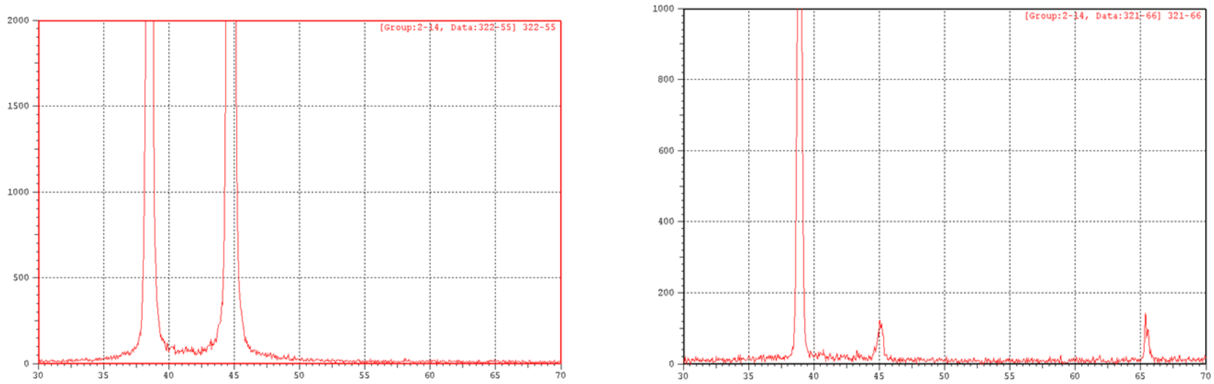
3.2.2. X-Ray Diffraction (XRD) Test

The XRD test were carried out on samples before and after laser surface melting as shown in Figure (5 a, b and c).



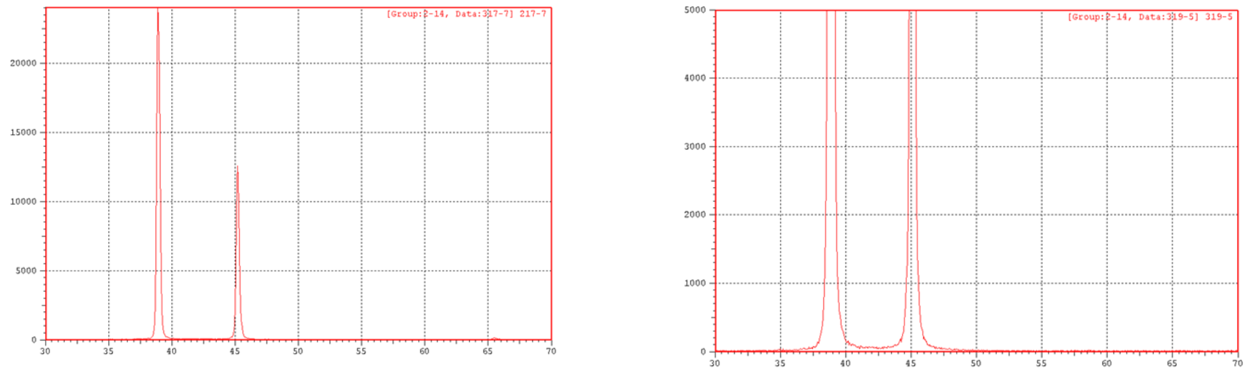
Before LSM After LSM

Figure (5) a) XRD test result for AA7075 before and after LSM



Before LSM After LSM

Figure (5) a) XRD test result for AA6061 before and after LSM



Before LSM After LSM

Figure (5) a) XRD test result for AA5083 before and after LSM

These Figures show that after laser surface melting, no intermetallic particles were evident, indicating a complete dissolution/removal of various intermetallic particles within the melted surface.

The results of XRD in these figures show that the surface of aluminum alloys becomes more homogenous and pure after treatment.

CONCLUSIONS

The results of the research performed yield the following conclusions:

- Potentiodynamic polarization tests show that the pitting potentialof the treated specimens shifts to more positive direction for all aluminum alloys in different concentrations of the NaCl solution.
- The potentiodynamic polarization results have shown that a result of the laser-treatment, the corrosion current was reduced by three times. As a consequence of this test the untreated sample is more susceptible to corrosion, while the laser-treated specimen is less susceptible to corrosion.
- A homogenous microstructure was verified as a result of rapid solidification and the results obtained in this study indicate a possibly more chemically stable phase, i.e. improved passive/oxide film after LSM treatment, which could serve as an effective barrier against corrosion attack in aggressive environments.
- The tests reveal that the untreated surface suffers from severe corrosion attacks, while the laser-treated surface is largely free from corrosion attacks. And Optical Microscope Pictures after the electrochemical corrosion tests show most corrosion damage in the untreated specimen whereas in the treated specimens the number of pits is reduced.
- Therefore, it can be concluded that LSM process indeed has an influence on surface film modification, which results in higher corrosion resistance.

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